of the absorption bands arising from the $NH_2$ stretching vibrations probably results from the fact that one of the hydrogen atoms of the amine group is bonded to the adjacent oxygen atom of the nitro group. As a result there is some uncertainty regarding the assignment of the 3500 cm.$^{-1}$ absorption band to the asymmetric $NH_2$ stretching vibration. However, since all of the absorption bands in the vicinity of 3500 cm.$^{-1}$ which could be assigned to this vibration have the same polarization characteristics as those bands due to known planar vibrations, the $NH_2$ group is assumed to be planar. This configuration would be expected for the $NH_2$ group in this case because of bonding and resonance.

o-Nitrobromobenzene.—The information listed in Table I for o-nitrobromobenzene, obtained from the spectra in Fig. 1D, illustrate the effect of a large ortho substituent upon the geometry of the nitro group. The absorption band at 1582 cm.$^{-1}$ arising from the asymmetric $NO_2$ stretching vibration is polarized in the same direction as the absorption bands due to non-planar vibrations and opposite to those from planar vibrations. Therefore, the plane of the nitro group is rotated well out of the plane of the benzene ring due to the steric influence of the adjacent bromine atom and is probably almost perpendicular to the ring. This steric effect is usually observed indirectly by measuring the change in properties (e.g., dipole moments, ultraviolet spectra, rates of reaction, etc.) resulting

from the inhibition of resonance[18] or by more direct X-ray diffraction methods.[15]

o-Nitrochlorobenzene.—The observed spectra of o-nitrochlorobenzene are given in Fig. 1E and the polarization data are presented in Table I. The absorption band at 1528 cm.$^{-1}$ corresponding to the asymmetric $NO_2$ stretching vibration has polarization characteristics more similar to the absorption bands from the non-planar rather than planar vibrations. Therefore, it is assumed that the plane of the nitro group is not coplanar with the benzene ring. The polarization of the 1528 cm.$^{-1}$ absorption band does not compare as closely to the 776 cm.$^{-1}$ band as for the analogous absorption bands in o-nitrobromobenzene. This difference may be assumed to indicate a smaller angle between the benzene ring and the nitro group in o-nitrochlorobenzene than in o-nitrobromobenzene, which would be expected because of the difference in van der Waals radii between chlorine and bromine. However, it is difficult to attempt such quantitative comparisons in view of the non-ideal nature of the preparations used.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# The Kinetics of Competitive Consecutive Second-order Reactions: The Saponification of Ethyl Adipate and of Ethyl Succinate[1]

BY ARTHUR A. FROST AND WARREN C. SCHWEMER

The differential rate equations for the kinetics of the reactions of the type $A + B \xrightarrow{k_1} C + E$ and $A + C \xrightarrow{k_2} D + E$ have been integrated for the special case of stoichiometrically equivalent amounts of the reactants A and B. Numerical tables and graphs have been prepared that enable (a) the determination of whether a reaction is of this kinetic type, and (b) the evaluation of the rate constants. Measurements of the rate of saponification of ethyl adipate and ethyl succinate have been made and used as an illustration of the application of the theory.

Competitive consecutive (series) second-order reactions, as usually exemplified by the saponification of diesters were first accurately handled by Ingold[2] who used a successive approximation method to obtain the rate constants. Ritchie[3] made use of a procedure of graphical differentiation while the work of Westheimer, Jones and Lad[4] involved graphical integration. French[5] has recently handled this kinetic problem in more general fashion but still requiring a graphical integration for each kinetic run.

The aim of the present work was to integrate this

kinetic system once and for all in terms of general variables that would apply to any future experimental results.

## Theoretical Treatment

The chemical equations of the system are

$$A + B \xrightarrow{k_1} C + E$$
$$A + C \xrightarrow{k_2} D + E$$
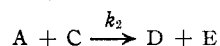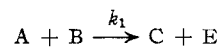
and the pertinent rate equations are

$$dA/dt = -k_1AB - k_2AC \qquad (1)$$
$$dB/dt = -k_1AB \qquad (2)$$
$$dC/dt = k_1AB - k_2AC \qquad (3)$$

where $A$, $B$ and $C$ represent the molar concentrations of the corresponding chemical species. Let the initial concentrations of A and B be $A_0$ and $B_0$, respectively, and the initial concentrations of C

(1) Abstracted in part from the Ph.D. thesis of Warren C. Schwemer at Northwestern University, August, 1950. Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951. See also W. C. Schwemer and A. A. Frost, THIS JOURNAL, 73, 4541 (1951).

(2) C. K. Ingold, J. Chem. Soc., 2170 (1931).

(3) M. Ritchie, ibid., 3112 (1931).

(4) F. H. Westheimer, W. A. Jones and R. A. Lad, J. Chem. Phys., 10, 478 (1942).

(5) D. French, THIS JOURNAL, 72, 4806 (1950).

and D both zero. From the principle of material balance

$$A - 2B - C = A_0 - 2B_0$$

Imposing for convenience the initial condition that $A_0 = 2B_0$ (equivalent amounts), then

$$C = A - 2B \qquad (4)$$

and equation (1) becomes after substitution

$$dA/dt = (2k_2 - k_1)AB - k_2A^2 \qquad (5)$$

The mathematical treatment is somewhat simplified by the introduction of the following dimensionless variables $\alpha$, $\beta$ and $\tau$ and parameter $\kappa$.

$$\alpha = A/A_0 \qquad \beta = B/B_0$$
$$\tau = B_0k_1t \qquad \kappa = k_2/k_1 \qquad (6)$$

In terms of these, equations (5) and (2) become

$$d\alpha/dt = (2\kappa - 1)\alpha\beta - 2\alpha^2 \qquad (7)$$
$$d\beta/d\tau = -2\alpha\beta \qquad (8)$$

Dividing (7) by (8) yields

$$\frac{d\alpha}{d\beta} = \frac{1 - 2\kappa}{2} + \kappa\frac{\alpha}{\beta} \qquad (9)$$

which is a linear differential equation with the solution

$$\alpha = \frac{1 - 2\kappa}{2(1 - \kappa)}\beta + \frac{1}{2(1 - \kappa)}\beta^\kappa \qquad (10)$$

where the constant of integration is determined by the initial condition that when $\alpha = 1$, $\beta = 1$. If (10) is substituted for $\alpha$ in (8) there results

$$\frac{d\beta}{d\tau} = -\beta^2\left[\frac{1 - 2\kappa}{1 - \kappa} + \frac{1}{1 - \kappa}\beta^{\kappa-1}\right]$$

or

$$\tau = \frac{1 - \kappa}{1 - 2\kappa}\int_\beta^1\frac{d\beta}{\beta^2\left(1 + \frac{1}{1 - 2\kappa}\beta^{\kappa-1}\right)} \qquad (11)$$

taking $\tau = 0$ at $\beta = 1$. The solution of the kinetic problem then involves the evaluation of the integral in (11) for various values of the limit $\beta$ and the parameter $\kappa$. The concentrations of the reactants and products can then be evaluated with the aid of equations (10), (6) and (2) and similar material balance equations for D and E if desired. See the appendix for details of the integration and numerical evaluation.

The results for $\alpha$ and $\beta$ as functions of $\tau$ are shown graphically in Figs. 1 and 2 and numerically in Table I for the most useful range of $\kappa$. $\tau$ is plotted on a logarithmic axis both to compress the time scale as well as to make possible the use of the Powell[6] method for evaluation of the rate constants from experimental data. Because $\tau$ is defined as $B_0k_1t$

$$\log \tau = \log B_0k_1 + \log t$$

Therefore if experimental values for $\alpha$ or $\beta$ are plotted against log $t$ a shift of the plot along the log $t$ axis by an amount log $B_0k_1$ should make the curve coincide with one of the infinite family of curves such as those in Fig. 1 or 2. From the shape of the curve $\kappa$ can be determined, at least approximately, and from this together with the shift log $B_0k_1$ both $k_1$ and $k_2$ can then be calculated. If the
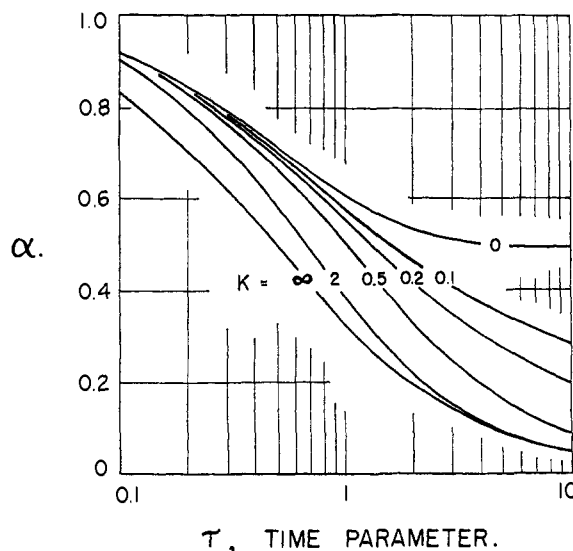
(6) R. Powell, private communication.



Fig. 1.—Plot of $\alpha$, fraction of substance A, as a function of the time parameter $\tau$ ($\tau = B_0k_1t$), for various values of $1/\kappa = k_2/k_1$.
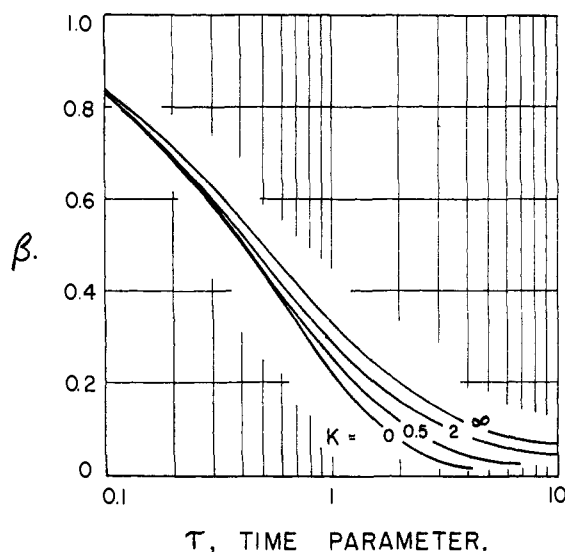


Fig. 2.—Plot of $\beta$, fraction of substance B remaining, as a function of the time parameter $\tau$ for various values of $1/\kappa = k_2k_1$.

experimental curve for $\alpha$ or $\beta$ fits one of the theoretical family of curves it may be supposed that the kinetics are probably of the type being discussed. However, caution must be used since for certain special values of $\kappa$ the dependence of $\alpha$ or $\beta$ on $\tau$ degenerates into what would correspond to a reaction of simple order, e.g., simple second order for $\kappa = 0$, $1/2$ or $\infty$.

Since $\kappa$ cannot be accurately determined by this curve-fitting procedure a better way was devised as follows. It will be noticed that the most distinctive effect of varying $\kappa$ is to change the slope of the curves of $\alpha$ or $\beta$ as a function of log $\tau$ in the neighborhood of $\alpha$ or $\beta$ equal to 0.5. Now the inverse of this slope is approximately given by $\Delta\log \tau/\Delta\alpha$ or taking in particular $\tau = \tau_{0.6}$ at $\alpha = 0.6$ and $\tau = \tau_{0.4}$ at $\alpha = 0.4$ the expression becomes

$$-5 \log (\tau_{0.4}/\tau_{0.6}) = -5 \log (t_{0.4}/t_{0.6})$$

## TABLE I
### τ AS A FUNCTION OF κ AND α

| 1/κ | α = 0.8 | 0.7 | 0.6 | 0.5 | 0.4 |
|---|---|---|---|---|---|
| 2.0 | 0.2500 | 0.4286 | 0.6667 | 1.000 | 1.500 |
| 2.2 | .2525 | .4354 | .6817 | 1.030 | 1.557 |
| 2.4 | .2547 | .4414 | .6953 | 1.058 | 1.613 |
| 2.6 | .2566 | .4468 | .7079 | 1.084 | 1.667 |
| 2.8 | .2583 | .4518 | .7195 | 1.109 | 1.719 |
| 3.0 | .2599 | .4564 | .7305 | 1.133 | 1.770 |
| 3.2 | .2612 | .4606 | .7407 | 1.156 | 1.820 |
| 3.4 | .2624 | .4643 | .7502 | 1.178 | 1.869 |
| 3.6 | .2636 | .4678 | .7591 | 1.199 | 1.917 |
| 3.8 | .2646 | .4711 | .7676 | 1.220 | 1.964 |
| 4.0 | .2656 | .4741 | .7756 | 1.239 | 2.011 |
| 4.2 | .2664 | .4769 | .7832 | 1.258 | 2.056 |
| 4.4 | .2672 | .4795 | .7903 | 1.276 | 2.102 |
| 4.6 | .2680 | .4820 | .7972 | 1.294 | 2.147 |
| 4.8 | .2687 | .4843 | .8037 | 1.311 | 2.191 |
| 5.0 | .2693 | .4865 | .8098 | 1.327 | 2.235 |
| 5.2 | .2699 | .4886 | .8156 | 1.344 | 2.278 |
| 5.4 | .2705 | .4906 | .8213 | 1.359 | 2.321 |
| 5.6 | .2711 | .4924 | .8267 | 1.374 | 2.364 |
| 5.8 | .2715 | .4941 | .8319 | 1.389 | 2.406 |
| 6.0 | .2720 | .4957 | .8368 | 1.404 | 2.449 |
| 6.2 | .2724 | .4973 | .8416 | 1.418 | 2.491 |
| 6.4 | .2728 | .4988 | .8463 | 1.432 | 2.532 |
| 6.6 | .2732 | .5002 | .8507 | 1.445 | 2.574 |
| 6.8 | .2736 | .5016 | .8549 | 1.458 | 2.615 |
| 7.0 | .2740 | .5028 | .8589 | 1.471 | 2.657 |
| 7.2 | .2743 | .5041 | .8629 | 1.484 | 2.698 |
| 7.4 | .2747 | .5053 | .8667 | 1.496 | 2.739 |
| 7.6 | .2750 | .5064 | .8704 | 1.508 | 2.780 |
| 7.8 | .2753 | .5075 | .8739 | 1.520 | 2.821 |
| 8.0 | .2755 | .5085 | .8773 | 1.531 | 2.862 |
| 8.2 | .2758 | .5095 | .8807 | 1.543 | 2.903 |
| 8.4 | .2761 | .5105 | .8839 | 1.554 | 2.944 |
| 8.6 | .2763 | .5114 | .8869 | 1.565 | 2.984 |
| 8.8 | .2765 | .5123 | .8899 | 1.576 | 3.026 |
| 9.0 | .2768 | .5131 | .8929 | 1.586 | 3.066 |
| 9.2 | .2770 | .5139 | .8957 | 1.597 | 3.108 |
| 9.4 | .2772 | .5147 | .8985 | 1.607 | 3.148 |
| 9.6 | .2774 | .5155 | .9012 | 1.617 | 3.189 |
| 9.8 | .2776 | .5162 | .9038 | 1.627 | 3.230 |
| 10.0 | .2778 | .5170 | .9064 | 1.637 | 3.270 |

since $B_0 k_1$ will cancel. It is apparent then that a ratio of the times for certain fractions of reactant



TIME RATIO.
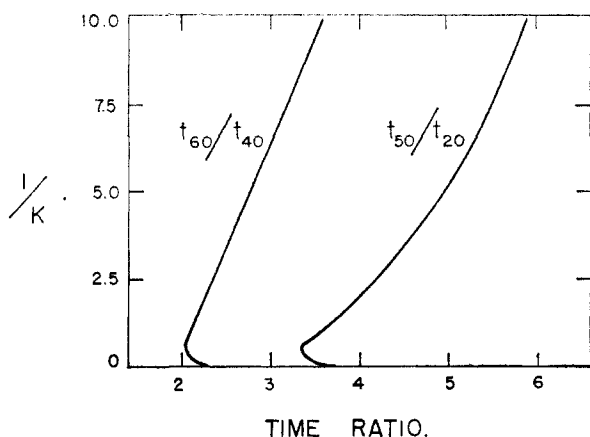
Fig. 3.—Plot of $1/κ$ *versus* the time ratio for 60 and 40% reaction and for 50 and 20% reaction, in terms of substance A.

remaining will be a function only of $κ$. Table II shows calculated values of various time ratios. Figure 3 is a graph of the data of Table II with certain extensions. In applying these results

## TABLE II
### TIME RATIOS AS A FUNCTION OF κ

$t_{60}/t_{20}$ is ratio of time for 60% A reacting to time for 20% reaction, or where $α = 0.4$ and $0.8$, respectively.

| 1/κ | $t_{60}/t_{40}$ | $t_{60}/t_{50}$ | $t_{60}/t_{80}$ | $t_{40}/t_{50}$ | $t_{50}/t_{20}$ | $t_{60}/t_{50}$ |
|---|---|---|---|---|---|---|
| 2.0 | 6.000 | 3.500 | 2.250 | 1.500 | 4.000 | 2.333 |
| 2.2 | 6.167 | 3.577 | 2.285 | 1.513 | 4.079 | 2.366 |
| 2.4 | 6.332 | 3.653 | 2.320 | 1.525 | 4.154 | 2.397 |
| 2.6 | 6.495 | 3.729 | 2.354 | 1.538 | 4.225 | 2.426 |
| 2.8 | 6.655 | 3.804 | 2.389 | 1.550 | 4.294 | 2.455 |
| 3.0 | 6.812 | 3.878 | 2.423 | 1.562 | 4.362 | 2.483 |
| 3.2 | 6.966 | 3.952 | 2.457 | 1.574 | 4.427 | 2.511 |
| 3.4 | 7.121 | 4.025 | 2.491 | 1.586 | 4.489 | 2.537 |
| 3.6 | 7.272 | 4.097 | 2.525 | 1.599 | 4.550 | 2.564 |
| 3.8 | 7.422 | 4.169 | 2.558 | 1.611 | 4.609 | 2.590 |
| 4.0 | 7.571 | 4.241 | 2.592 | 1.623 | 4.666 | 2.614 |
| 4.2 | 7.718 | 4.312 | 2.626 | 1.635 | 4.722 | 2.638 |
| 4.4 | 7.864 | 4.383 | 2.659 | 1.647 | 4.776 | 2.662 |
| 4.6 | 8.010 | 4.453 | 2.693 | 1.660 | 4.828 | 2.684 |
| 4.8 | 8.154 | 4.523 | 2.726 | 1.672 | 4.878 | 2.706 |
| 5.0 | 8.297 | 4.593 | 2.760 | 1.684 | 4.928 | 2.728 |
| 5.2 | 8.439 | 4.663 | 2.793 | 1.696 | 4.978 | 2.750 |
| 5.4 | 8.581 | 4.732 | 2.827 | 1.709 | 5.025 | 2.771 |
| 5.6 | 8.723 | 4.801 | 2.860 | 1.721 | 5.071 | 2.792 |
| 5.8 | 8.863 | 4.871 | 2.894 | 1.733 | 5.117 | 2.812 |
| 6.0 | 9.003 | 4.940 | 2.927 | 1.745 | 5.161 | 2.832 |
| 6.2 | 9.143 | 5.009 | 2.961 | 1.757 | 5.205 | 2.851 |
| 6.4 | 9.283 | 5.078 | 2.994 | 1.769 | 5.249 | 2.870 |
| 6.6 | 9.421 | 5.147 | 3.027 | 1.782 | 5.290 | 2.888 |
| 6.8 | 9.559 | 5.216 | 3.061 | 1.794 | 5.330 | 2.960 |
| 7.0 | 9.698 | 5.285 | 3.094 | 1.806 | 5.369 | 2.925 |
| 7.2 | 9.836 | 5.354 | 3.128 | 1.819 | 5.407 | 2.943 |
| 7.4 | 9.974 | 5.422 | 3.162 | 1.831 | 5.445 | 2.961 |
| 7.6 | 10.112 | 5.491 | 3.196 | 1.844 | 5.485 | 2.977 |
| 7.8 | 10.250 | 5.560 | 3.229 | 1.856 | 5.521 | 2.995 |
| 8.0 | 10.388 | 5.629 | 3.263 | 1.869 | 5.558 | 3.012 |
| 8.2 | 10.526 | 5.698 | 3.297 | 1.882 | 5.594 | 3.028 |
| 8.4 | 10.664 | 5.767 | 3.332 | 1.895 | 5.629 | 3.044 |
| 8.6 | 10.802 | 5.836 | 3.366 | 1.908 | 5.663 | 3.060 |
| 8.8 | 10.940 | 5.905 | 3.400 | 1.920 | 5.697 | 3.076 |
| 9.0 | 11.078 | 5.975 | 3.434 | 1.933 | 5.731 | 3.091 |
| 9.2 | 11.216 | 6.045 | 3.469 | 1.946 | 5.765 | 3.106 |
| 9.4 | 11.354 | 6.115 | 3.503 | 1.959 | 5.797 | 3.122 |
| 9.6 | 11.492 | 6.185 | 3.538 | 1.972 | 5.829 | 3.137 |
| 9.8 | 11.632 | 6.255 | 3.573 | 1.985 | 5.861 | 3.152 |
| 10.0 | 11.772 | 6.325 | 3.607 | 1.998 | 5.892 | 3.166 |

to experimental data the procedure is to obtain several independent values of $κ$ from various experimental time ratios and to inspect the $κ$ values for constancy using data from either a single kinetic run or several runs. After obtaining $κ$ reference is then made to Table I where for several values of $\%$ reaction $τ$ can be accurately found which then by comparison with experimental $t$ and $B_0$ values will yield values of $k_1$.

**Application of the Theory to Experimental Results.**—A search of the literature revealed no data with which a satisfactory comparison with the theoretical results described here could be made. Either the initial conditions did not correspond to those considered here, namely, equiv-

alent concentrations, or the extent of reaction was not sufficiently great. Therefore measurements of the rates of saponification of ethyl adipate and ethyl succinate by sodium hydroxide were made.

The usual titration procedure for following saponifications was used with certain modifications. Samples of the reaction mixture were pipetted at measured time intervals into a solution containing an excess of potassium acid phthalate which served to stop the reaction. This acid was used rather than hydrochloric or other strong acid because it provided fewer hydrogen ions to catalyze either the forward or reverse reactions and also because it provided a better end-point in the titrations. Carbon dioxide was carefully removed from the original solvents and kept from the system during reaction and titrations by a stream of nitrogen. The sodium hydroxide used for the reacting system and for the titrations was prepared carbonate-free by the reaction of sodium with water. The esters were obtained as the best grade of Eastman Kodak Co. chemicals and purified by an adsorption column. Their purities were tested by their saponification equivalents which yielded molecular weights of 174.4 and 202.2 for the succinate and adipate, respectively, as compared with the calculated molecular weights of 174.19 and 202.25. The solvent used was a one to three volumetric ratio of dioxane and water which was made 0.2000 $N$ in potassium chloride, this latter being included so as to swamp out any effects due to changes in ionic strength that would occur as the diacid ion was produced. Further details of technique and apparatus may be found in reference 1.

## Results

Three kinetic runs were made on each of the esters. Run No. 1 on ethyl adipate as shown in Table III is typical of the results.

### TABLE III

RATE OF SAPONIFICATION OF ETHYL ADIPATE WITH SODIUM HYDROXIDE IN DIOXANE–WATER–POTASSIUM CHLORIDE SOLUTION

Run No. 1: initial concentration of reactants, 0.00996 $N$; normality of sodium hydroxide for titrating, 0.01057 $N$. Normality of potassium acid phthalate, 0.01497 $N$; volume of sample, 9.98 ml.; volume of potassium acid phthalate solution, 9.99 ml.; temperature, 25.00°.

| Time in seconds | NaOH in titration, ml. | $[OH^-]$, $N$ | $\alpha = [OH^-]/[OH^-]_0$ |
|---|---|---|---|
| 0 | ... | 0.00996 | 1.0000 |
| 165 | 5.36 | .00931 | 0.935 |
| 370 | 5.99 | .00864 | .868 |
| 510 | 6.39 | .00822 | .825 |
| 628 | 6.68 | .00791 | .794 |
| 757 | 6.97 | .00760 | .763 |
| 965 | 7.36 | .00719 | .722 |
| 1180 | 7.77 | .00676 | .679 |
| 1357 | 8.03 | .00648 | .651 |
| 1671 | 8.49 | .00599 | .601 |
| 2062 | 8.93 | .00553 | .555 |
| 2468 | 9.33 | .00510 | .512 |
| 3077 | 9.84 | .00456 | .458 |
| 3664 | 10.18 | .00420 | .422 |
| 4466 | 10.60 | .00376 | .378 |
| 5271 | 10.94 | .00340 | .341 |

Table IV shows the results of calculation of $1/\kappa$ and $k_1$ and $k_2$. $\alpha$ is first plotted as a function of $t$ on a large scale. From a smooth curve drawn through the experimental points the times for 20% up to 60% reaction are read. From the $t$ ratios the corresponding $1/\kappa$'s are found by interpolating in Table II and then after taking the average the values of $\tau$ and $k_1$ are then determined using Table I.

### TABLE IV

CALCULATIONS OF RATE CONSTANTS FOR RUN No. 1 ON ETHYL ADIPATE

| % Rx. | $t$, sec. | Percentages compared | $t$ ratio | $1/\kappa$ |
|---|---|---|---|---|
| 20 | 605 | 60/20 | 6.661 | 2.808 |
| 30 | 1060 | 60/30 | 3.802 | 2.795 |
| 40 | 1690 | 60/40 | 2.385 | 2.777 |
| 50 | 2595 | 60/50 | 1.553 | 2.850 |
| 60 | 4030 . | 50/20 | 4.289 | 2.785 |
|  |  | 50/30 | 2.448 | 2.750 |

Average $1/\kappa$ = 2.79

| % Rx. | $\tau$ | $k_1$ l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|
| 20 | 0.2582 | 0.08570 |
| 30 | 0.4516 | .08555 |
| 40 | 0.7189 | .08542 |
| 50 | 1.108 | .08574 |
| 60 | 1.716 | .08550 |

Average $k_1$ = 0.0856    $k_2$ = 0.0856/2.79 = 0.0307 l. mole$^{-1}$ sec.$^{-1}$

Table V summarizes the rate constants for the six runs. It may be concluded that the values are good to within 0.2 to 0.3%. Table VI shows how

### TABLE V

SUMMARY OF RATE CONSTANTS FOR THE SAPONIFICATION OF DIESTERS BY SODIUM HYDROXIDE

| Run No. | Initial concn., $N$ | $k_1$, l. mole$^{-1}$ sec.$^{-1}$ | $k_2$, l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|
|  | Ethyl adipate |  |  |
| 1 | 0.00996 | 0.0856 | 0.0307 |
| 2 | .00986 | .0856 | .0304 |
| 3 | .00902 | .0855 | .0305 |
|  | Average | 0.0856 | 0.0305 |
|  | Ethyl succinate |  |  |
| 1 | 0.00988 | 0.190 | 0.0354 |
| 2 | .00903 | .190 | .0352 |
| 3 | .00823 | .191 | .0352 |
|  | Average | 0.190 | 0.0353 |

### TABLE VI

COMPARISON OF RATE CONSTANTS FOR THE SAPONIFICATION OF DIESTERS BY SODIUM HYDROXIDE

| Investigators | Solvent | Temp., °C. | $k_1$ liters | $k_2$ mole$^{-1}$ min.$^{-1}$ |
|---|---|---|---|---|
|  | Ethyl adipate |  |  |  |
| Ingold | Water | 20.3 | 3.52 | 0.704 |
| Westheimer, Jones and Lad (extrapolated) | Water | 20.0 | 5.97 | 1.23 |
| This research | Water, dioxane, KCl | 25.0 | 5.14 | 1.83 |
|  | Ethyl succinate |  |  |  |
| Ingold | Water | 20.3 | 12.05 | 1.253 |
| Ritchie | Water | 25.0 | 12.3 | 1.93 |
| This research | Water, dioxane, KCl | 25.0 | 11.4 | 2.12 |

these rate constants relate to those of other investigators. It must be realized that because of differences in solvents and temperatures there is no direct comparison.

**Acknowledgment.**—We are indebted to the Standard Oil Company of Indiana for a fellowship held by the junior author during a portion of this research.

## Appendix

The integral of equation (11) may be evaluated for certain ranges of $\kappa$ as follows:

### Case I.   $0 < \kappa < \frac{1}{2}$

Let $\kappa = m/n$ where $m$ and $n$ are both integers and $n > 2m$. This situation is most common since for the saponification of symmetrical diesters $k_1$ will always be at least $2k_2$ purely on statistical grounds and will be greater than $2k_2$ due to repulsive effects between the hydroxide ion and the half-ester ion. By substitution

$$\tau = \frac{(1 - \kappa)}{(1 - 2\kappa)} \int_\beta^1 \frac{d\beta}{\beta^2 \left(1 + \frac{n}{n - 2m} \beta^{(m-n)/n}\right)}$$

Let $x = \left(\frac{n}{n - 2m}\right)^{\frac{1}{m-n}} \beta^{-1/n}$   then

$$\tau = (1 - \kappa)(1 - 2\kappa)^{\frac{1}{1-\kappa}} n \int_{x_0}^x \frac{x^{n-1}}{x^{n-m} + 1} dx \quad (12)$$

where

$$x_0 = \left(\frac{n}{n - 2m}\right)^{\frac{1}{n-m}}$$

The integral over $x$ is of the general form

$$\int \frac{x^p}{x^q + 1} dx$$

which for $p > q$ may be simplified to

$$\int \frac{x^p}{x^q + 1} dx = \frac{1}{p - q + 1} x^{p-q+1} - \int \frac{x^{p-q}}{x^q + 1} dx \quad (13)$$

For $p < q$ the integral may be evaluated by the use of partial fractions and the result is[7]

$$\int \frac{x^p}{x^q + 1} dx = (-1)^p \frac{s}{q} \log (x + 1) -$$

$$\frac{2}{q} \sum_{\nu=0}^{q-1} \left[ P_\nu \cos \frac{(2\nu + 1)(p + 1)\pi}{q} - Q_\nu \sin \frac{(2\nu + 1)(p + 1)\pi}{q} \right] + C \quad (14)$$

with $q = 2r + s$; $s = 0$ or $1$; $p = 0, 1, \cdots q - 1$

$$P_\nu = \frac{1}{2} \log \left( x^2 - 2x \cos \frac{2\nu + 1}{q} \pi + 1 \right)$$

$$Q_\nu = \arctan \left( \frac{x - \cos \frac{2\nu + 1}{q} \pi}{\sin \frac{2\nu + 1}{q} \pi} \right)$$

The calculated values of Table I were obtained in this way for $\kappa = \frac{1}{2}, \frac{4}{9}, \frac{2}{5}, \frac{1}{3}, \frac{2}{7}, \frac{1}{4}, \frac{2}{9}, \frac{1}{5}, \frac{1}{6}, \frac{1}{7}, \frac{1}{8}, \frac{1}{9}$ and $\frac{1}{10}$.

An interpolation was then made for every 0.2 for $1/\kappa$ from 2.0 to 10.0. In these calculations

tables of arctangent and natural logarithms were particularly useful.[8]

### Case II:   $\frac{1}{2} < \kappa < \infty$ , $\kappa \neq 1$

Let $\kappa = m/n$ as before, but let

$$x = n \left(\frac{n}{2m - n}\right)^{\frac{1}{n-m}} \beta^{-1/n}; \text{ then}$$

$$\tau = (1 - \kappa)(2\kappa - 1)^{\frac{1}{1-\kappa}} n \int_{x_0}^x \frac{x^{n-1} dx}{x^{n-m} - 1} \quad (15)$$

with the lower limit now

$$x_0 = \left(\frac{n}{2m - n}\right)^{\frac{1}{n-m}}$$

The integral over $x$ is of the general form

$$\int \frac{x^p}{x^q - 1} dx$$

which for $p > q$ may be reduced as

$$\int \frac{x^p}{x^q - 1} dx = \frac{1}{p - q + 1} x^{p-q+1} + \int \frac{x^{p-q}}{x^q - 1} dx \quad (16)$$

For $p < q$ the integral is[7]

$$\int \frac{x^p}{x^q - 1} dx = \frac{1}{q} \log (x - 1) +$$

$$\frac{(1 - s)(-1)^{p+1}}{q} \log (x + 1) +$$

$$\frac{2}{q} \sum_{\nu=1}^{q-1} \left[ R_\nu \cos \frac{2\nu(p + 1)}{q} \pi - S_\nu \sin \frac{2\nu(p + 1)}{q} \pi \right] + C \quad (17)$$

with $q = 2r - s$; $s = 0$ or $1$; $q > 2$; $p = 0,1 \cdots q - 1$

$$R_\nu = \frac{1}{2} \log \left( x^2 - 2x \cos \frac{2\nu\pi}{q} + 1 \right)$$

$$S_\nu = \arctan \left( \frac{x - \cos \frac{2\nu\pi}{q}}{\sin \frac{2\nu\pi}{q}} \right)$$

When $m > n$ the exponent in the denominator becomes negative and the integral may be expressed as

$$\int \frac{x^{n-1} dx}{x^{n-m} - 1} = -\frac{1}{n} x^n - \int \frac{x^{n-1}}{x^{m-n} - 1} dx + C \quad (18)$$

### Special Cases

For $\kappa = 0$ the reaction is a simple second-order reaction with the solution

$$\tau = \ln \left(\frac{\beta + 1}{2\beta}\right) \quad \text{and} \quad \alpha = \left(\frac{\beta + 1}{2}\right)$$

For $\kappa = \frac{1}{2}$ the reaction behaves as one of simple second-order as far as A is concerned

$$\tau = \frac{1}{\alpha} - 1 \quad \text{and} \quad \alpha^2 = \beta$$

For $\kappa = 1$

$$\tau = \frac{1}{e^2} \int_2^x \frac{e^x}{x} dx$$

where

$$x = 2 - \ln \beta$$

(7) W. Gröbner and N. Hofreiter, "Integraltafel," 1, Springer-Verlag, Vienna, 1949.

(8) "Project for Computation of Mathematical Tables," Federal Works Agency, A. N. Lowan, Technical Director, 1941–1942, New York, N. Y.

or

$$\tau = \frac{1}{e^2} [E_i (2 - \ln \beta) - E_i (2)]$$

where $Ei(x)$ is the Integral Logarithm function.

For $\kappa = \infty$ the reaction again behaves as one of

simple second order but here with the solution

$$\tau = \frac{1}{2} \left( \frac{1}{\beta} - 1 \right) \quad \text{and } \alpha = \beta$$

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# Experiments on Compound Formation in Solutions at Low Temperatures. Iodine and Olefins[1]

BY SIMON FREED AND KENNETH M. SANCIER

Absorption spectra of solutions of iodine in olefins at temperatures from 77 to 230°K. show the presence of ultraviolet bands which match those of iodine in aromatic hydrocarbons previously reported. These bands had been proved characteristic of 1:1 molecular addition compounds between iodine and the hydrocarbons. Such addition compounds are formed by iodine with each of the following olefins examined either pure or dissolved in propane: propene, cis-butene-2, trans-butene-2, butadiene-1,3, 2-methylbutadiene-1,3. Cyclopropane also combines with iodine in the same way in agreement with the double-bond character often attributed to it. The addition compounds form reversibly. However, they require activation energy. At higher temperatures another type of reaction sets in decolorizing the iodine solutions, probably the halogenation across the double bond. Especially good evidence that the addition compound is an intermediate in the halogenation of the double bond is furnished by 2-methylbutadiene-1,3 and iodine. The heats of formation of the addition compound vary from 200 to 500 cal./mole. The nature of the bond in these compounds is discussed.

It is to be expected that compounds may form and persist at low temperatures which at higher temperatures would not be present in detectable quantities. The lower temperatures may therefore make possible the observation of weakly bonded substances and permit the study of reaction intermediates. We report here phenomena of this kind in reactions between olefins and iodine. In these systems we also have examples of the reduction to be generally expected in the number of competing reactions when the temperature is reduced.

Solutions of iodine in organic solvents have often been classified into those which give purple and those which give brown solutions, with the former exemplified for our purpose by iodine in hexane and the latter by its solutions in aromatic solvents such as benzene. Benesi and Hildebrand[2] have shown that in addition to the absorption band in the visible region, the brown solutions possess an extremely intense absorption peak in the ultraviolet and that this peak is to be ascribed to a 1:1 complex between iodine and the aromatic hydrocarbon. They regarded such a complex as a Lewis salt between the generalized acid and base, iodine and aromatic hydrocarbon, respectively.

Mulliken[3] viewed the intense absorption peak in the ultraviolet as a forbidden transition between the energy levels of the aromatic conjugated double-bond system made allowed by the presence of iodine.

Our experiments to discover whether olefins also enter into what we shall call addition compounds were carried out at low temperatures to increase their concentration and to avoid the well-known reactivity of halogens for the "double bond" at room temperature.

A double-beam Cary spectrophotometer was employed for measuring the spectra of the solutions in fused quartz tubes with light paths of 1 and of 8 mm. To eliminate the optical effect of the fused quartz, refrigerant, solvent, etc., the tubes were also measured with all but iodine present.

The iodine dried over phosphorus pentoxide was dropped into a tube previously filled with dried nitrogen. The tube was then evacuated while the iodine was kept at 193°K. By allowing the temperature to rise, the iodine was sublimed several times onto the surface of another part of the tube kept at 193°K. and any released gases were pumped off. The final sublimate was obtained as a film. The propane[4] was condensed upon the iodine at 193°K. Some time was required to form the purple solution. The corresponding condensation of propene led at once to a brown solution at the interface between the iodine and propene which quickly diffused into the body of the liquid.

The solutions in propane and also in propene were obtained easily as supercooled fluids at the temperature of liquid nitrogen. Solutions in mixtures of these hydrocarbons appear to be stable fluids even below the freezing point of nitrogen.[5]

All our operations were carried out in dim light to reduce any photochemical activity.

**Propene and Propane.**—At 230°K. the color of iodine in propane is purple with an absorption peak at 5200 Å. while its solution in propene is amber with a peak at 4800 Å. At 77°K. both solutions have about the same brown color and the absorption peak of the propene solution is at 4400 Å. We are uncertain of the position of the peak of the propane solution because at our concentration there was evidence of colloidal iodine at this temperature. The area "under" the visible band of iodine–propane changes little with temperature but that of iodine–propene increased two to three-fold when the temperature was reduced from 230 to 77°K. (Fig. 1). In the ultraviolet region, the iodine–propene solution at 230°K. exhibited no structure down to 2100 Å. but the iodine–propene solution showed a band at 2750 Å. about ten times as intense as its absorption in the visible. Both the intensity and wave length of the ultraviolet absorption match those of iodine in aromatic solvents as given by Benesi and Hildebrand and there seems no doubt that it arises from a corresponding iodine–propene addition compound.

At 230°K., our highest temperature, an irreversible reac-

(1) Presented at the American Chemical Society Meeting, Chicago, Ill., September, 1950. Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, 71, 2703 (1949).

(3) R. S. Mulliken, ibid., 72, 600 (1950). At the Chicago Meeting of the A.C.S., September, 1950, he presented a more general interpretation.

(4) All the hydrocarbons except cyclopropane were research grade (Phillips Petroleum Co.) further fractionated several times by distillation. Cyclopropane was obtained from Matheson Co., several times distilled from its solution of iodine.

(5) S. Freed and C. J. Hochanadel, J. Chem. Phys., 17, 664 (1949).